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Natural Contamination by As and Heavy Metals in Soil, Their Bio-Accumulation and Potential Sources: the Case of a Travertine Limestone Quarry, Greece

Research Article

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Abstract: The first mineralogical and geochemical investigation of the travertine limestone, soil and corresponding plants associated with the Neogene basin of Varnavas, NE Attica, revealed a significant enrichment in the metalloid As. The total concentrations of As ranged from 61 to 210 ppm in limestone and 33 to 430 ppm in the associated soil demonstrating a wide variation of values. Calcite is a common authigenic mineral within travertine limestone, forming fine uniform micritic aggregates, having As and Mg concentrations lower than detection limits of EDS analysis. Clastic dominated minerals are quartz (both fine- and coarse-grained), muscovite, clinochlore, illite, pyrite, galena, arsenides, rutile, sphene, zircon, REE-minerals and albite. Goethite and Fe-Mn-oxides occur between calcite grains. The presence of fossilized micro organisms, resembling foraminifera, in travertine limestone combined with hydrous Fe-Mn-oxides, suggests a possible marine transgression during the evolution of the basin.

The As content in plants ranges from 1.1 to 28 ppm As in shoots, and 0.8 to 114 ppm As in roots. The translocation factor, which is defined as the ratio of metal concentration in the shoots to the roots, is relatively low (average 0.33%) suggesting that the internal transport of metals from the roots to shoots was restricted. The bioaccumulation factor, which is defined as the ratio of metal concentration in the plants to that in soil, exhibits a wide range from relatively low (5.2 - 9.0% for As, Fe, Cr, Ni and Pb), much higher (56 - 67% for Cu and Zn) and exceptionally high (160% for Mo). A significant correlation between the translocation factors for Fe and As may confirm that Fe-Mn oxides/hydroxides represent the major sorbing agents for As in soils. The presented data, due to As contamination in travertine limestone, soil and plants, suggest a potential environmental risk not only for that part of Greece but in general for similar depositional environments.

Keywords: arsenic• travertine limestone• Fe-Mn oxides• Mn-Fe ore• plants• Varnavas• Greece

1. Introduction

Arsenic (As) is a toxic and carcinogenic element, depending on its oxidation state. Elevated arsenic concentrations in nature may be derived by natural processes, such as the occurrence of arsenic in

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groundwater related to the presence of geothermal systems or to water-rock interactions, under specific geochemical conditions [1]. Also industrial activities such as mining of coal and mixed sulphides, smelting, beneficiation activities and a wide variety of applications can be responsible for the arsenic contamination [2–4]. It is well known that hazardous wastes may be highly toxic, with high bioavailable fractions of heavy metals, which may be transported over long distances and contaminate large agricultural areas [5–7]. Thus, toxic elements can be taken up by plants and finally enter the food chain, with adverse effects on human health. The European Union has adopted maximum levels for heavy metals as regards foodstuffs (Regulation 1881/2006/EK), drinking water (Directive 98/83/EK), and the use of sludge (Directive 86/278/EK), air (Directive 2008/50/EK) and tail gas incineration (Directive 2000/76/EK).

The present study is focussed on the first assessment of the arsenic content in a multicolour travertine limestone quarry, that may be a "risk lithology" for increased natural As concentrations in soils and plants, due to the vicinity with an abandoned Fe-Mn mine. The term travertine is commonly used in a broader sense, including all non-marine limestones formed under climatic controls in streams, lakes and springs. A great variety of travertine deposits have been described, depending on many variables, such as physical and biological processes [8]. Travertine, consisting of calcite or aragonite of low to moderate porosity, is generally defined as a chemically-precipitated continental limestone formed around seepages, springs and along streams, rivers and occasionally in lakes [9] has been located at the Varnavas basin, Attica, of Greece [10, 11]. This Neotectonic basin, composed of post-Alpine sediments including Late Miocene-Pliocene continental deposits and minor outcrops of Pleistocene and Holocene alluvial travertine limestones [10], is well known as an open quarry producing multicolored (yellow-orange-brown) travertine limestone, which is used as building material (Fig. 2). Preliminary investigation of the mineralogical, geochemical and mineral chemistry data on the Varnavas limestone basin revealed the presence of 2-4 hundreds of ppm arsenic (As) and significant heavy metal contents, such as copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), zinc (Zn) in soil and the associated travertine limestone [12].

In this study the investigation of the As, Mo, Cu, Pb, Zn, Mn, Fe, Sb and Hg contents in travertine limestone from the Varnavas quarry was extended to the wider area of the Kalamos basin (Fig. 1). A compilation of rock data, as well as the distribution of the above elements around the Varnavas travertine limestone quarry in soil and corresponding plants are presented, in order to provide the first assessment of the extent and intensity of their environmental impact, determine the As-hosts, metal bio-accumulation (their percentage transferred from soil into the plants) and the potential sources of contamination.

2. Geotectonic outline of the Varnavas basin

The basins being investigated, i.e. the Varnavas and Kalamos basins are located in NE Attica, between latitudes 23°85′ and 23°96′, and longitudes 38°16′ and 38°29′ (WGS84 system). The Varnavas basin covers approximately 30 km^2 [13] and the maximum altitude in the basin is 600 m, while it falls to 220 m towards Lake of Marathonas. Many coastal sites in the central Aegean region, including Attica, have followed the long-term subsidence trend of the Aegean Sea from the Middle to Upper Pleistocene and are characterized by an extensional tectonic regime [14]. A spatial distribution of uplift and subsidence in the coastal areas of the Aegean Sea has been demonstrated, as well as a relationship between this distribution and tectonic and sedimentary processes operating within the Aegean region [15].

East Attica is composed by two major units: (a) The lower group of the NE Attica comprising the autochthonous unit or crystalline basement, forming a large anticline with the axis oriented in the NNE-SSW direction, composed of metamorphic rocks (Triassic schists, metabasic, quartz-feldspathic rocks) and (b) an overlying carbonate sequence, ranging from upper Triassic to Upper Cretaceous and Neogene-Quaternary deposits [11] (Fig. 1). More specifically, the upper group, known as allochthonous metamorphic unit of Aghios Georgios, consists of glaucophane-bearing metasediments, metasandstones, calc-schists and mica blueschist intercalated with marble (Fig. 1) [11]. The Neogene formations, comprising Late Miocene-Pliocene continental deposits and minor Pleistocene and Holocene alluvial deposits, can be classified as follows: 1) continental deposits of clays, sandstones and conglomerates 2) lacustrine deposits of travertine limestones, located in the Varnavas and Kalamos basins 3) Continental deposits of conglomerates containing boulders. A large part of the Varnavas basin is covered by ririverine flood deposits [10].

The composition of the travertine limestone in the Varnavas basin may have been affected by transportation and deposition of the weathered material from the Grammatiko Fe-Mn mineralization. Although any continuity between the famous ancient mines of Grammatiko and Lavrio is not obvious, underground

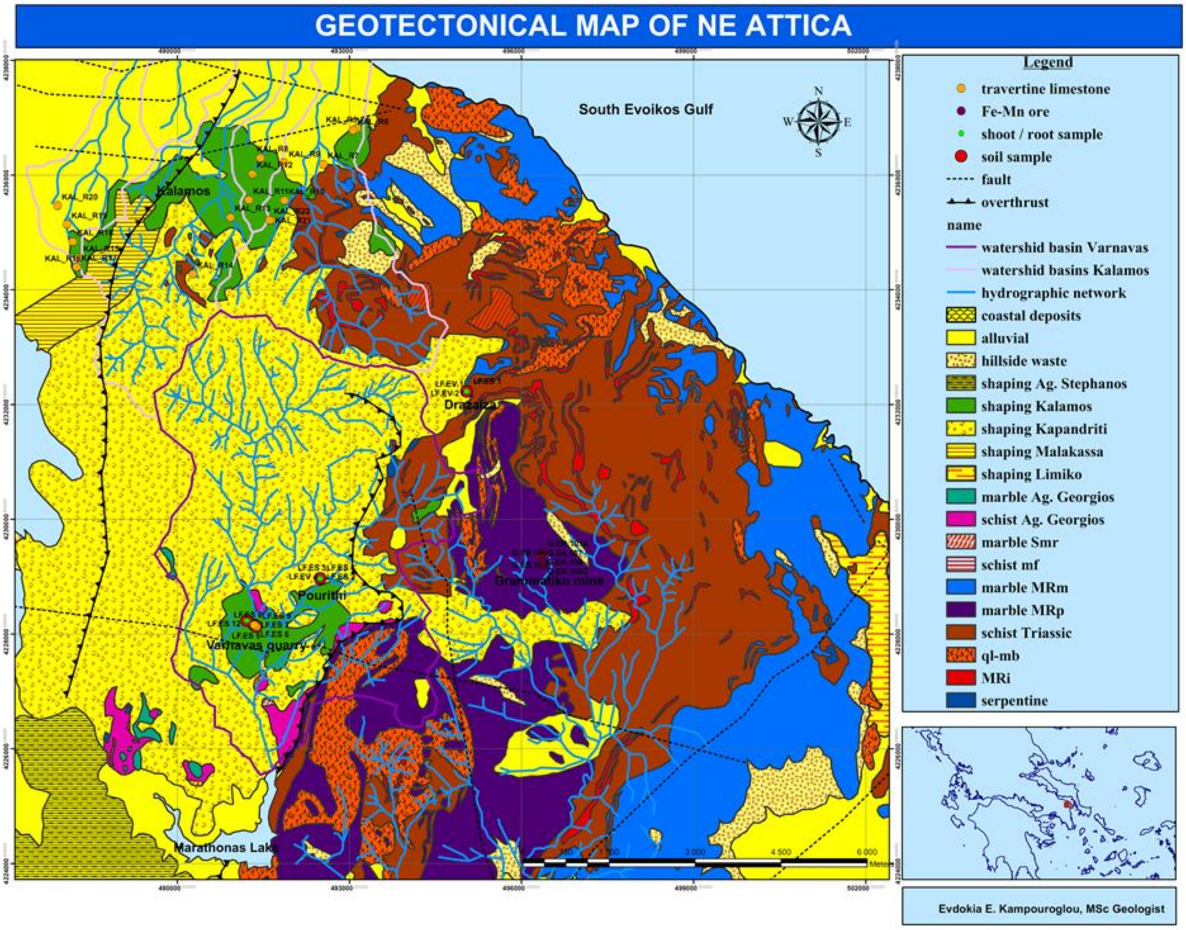


Figure 1. Simplified geotectonic map of NE Attica showing the localities of sampling.

Figure 2. Field view of the Varnavas quarry showing travertine limestone.

mining at Grammatiko revealed geological and structural relationships between the host rocks and the "ferromanganese formation" [16] or gossan [17] that resemble those located at the Lavrio mine.

3. Materials and Methods

The soil samples were collected mainly from the Varnavas Quarry, and only a few samples from the areas of Drazaiza and Pourithi (Fig. 1). Representative soil samples were collected from the rhizosphere of plants (during October 2010) from a maximum depth of approximately 20 cm in order to investigate probable relationships between element contents in plants and soil chemistry. In addition, representative samples of travertine limestone from the Varnavas quarry, Kalamos basin and around the abandoned Fe-Mn mine of Grammatiko were collected and analyzed.

The vegetation of NE Attica is composed of forests of

Table 1. Major and trace element contents in soils and travertine limestone from the Varnavas basin and Kalamos basins.

Sample					ppm							(wt%)		
Soils	As	Mo	Cu	Pb	Zn	Mn	Sb	Hg	Ba	Sr	Fe	P	Ca	Al	Organic matter
LF.ES1	33	0.6	39	14	64	940	0.4	0.01	43	55	3.4	0.08	13.0	1.9	4.1
LF.ES2	45	0.5	20	66	120	410	2.5	0.03	87	35	2.1	0.04	11.3	1.5	5.7
LF.ES3	47	0.5	16	63	110	310	2.8	0.04	67	46	1.8	0.04	16.7	1.0	6.7
LF.ES4	36	0.3	15	41	80	300	1.9	0.01	60	65	1.6	0.03	17.6	0.9	4.2
LF.ES5	270	1	19	64	180	700	7.3	0.13	72	40	2.4	0.02	14.7	0.9	1.3
LF.ES6	300	0.9	18	84	240	640	6.1	0.19	72	33	2.4	0.02	18.9	0.9	1.4
LF.ES7	320	1	19	63	240	590	6.6	0.18	65	40	2.3	0.03	19.2	0.7	1
LF.ES9	230	0.8	18	50	160	630	4.8	0.18	79	42	2.2	0.02	16.5	0.7	0.9
LF.ES12	220	2.2	21	15	39	450	3.7	0.03	44	40	2.7	0.03	14.3	0.9	0.6
LA.F.S.B	190	0.6	33	64	150	900	4.1	0.07	90	31	3.1	0.1	8.0	1.4	1.7
KAP-L-F	290	1	32	64	180	1000	7.5	0.03	93	22	3.8	0.05	6.8	1.5	0.9
KAP-L-FA	290	0.9	29	64	170	840	6	0.14	90	20	3.6	0.04	6	1.5	1.1
KAP-L-FB	290	1	30	64	180	980	7.7	0.04	87	22	3.6	0.05	6.7	1.5	1.1
LF.ES8	360	0.9	23	86	260	710	7	0.21	74	33	2.9	0.02	17.5	1.0	1.4
LF.ES10	340	0.9	23	62	220	610	7	0.17	66	41	2.9	0.03	14.7	0.9	1
LF.ES11	430	1	31	65	250	720	7.1	0.22	85	37	3.6	0.04	14.2	1.3	1.6
Average	231	0.9	24	58	165	671	5.2	0.1	73.4	37.6	2.8	0.04	13	1	2.1
Travertine	Limestone														
LF.ER1	61	1.5	5.1	43	87	2400	1.9	0.2	432	60	0.3	0.01	37	0.20	0.14
LF.ER2	102	0.3	5.6	51	130	210	2.7	0.2	42	39	0.7	0.01	32	0.29	0.31
LF.ER3	34	0.3	2.8	78	100	260	1.7	0.2	56	64	0.3	0.01	33	0.19	0.26
LA.F.S.K	210	2	14	190	270	1400	7.6	0.3	200	49	1.2	0.02	36	0.20	0.21
KAL-R5	31	0.05	1.1	1.1	30	4	0.1	0.01	13	53	0.1	0.003	32	0.01	0.10
KAL-R6	33	0.05	1.9	4.2	40	20	0.2	0.01	12	45	0.2	0.004	35	0.05	0.12
KAL-R7	29	0.05	0.8	0.7	7	23	0.1	0.01	11	48	0.2	0.002	34	0.01	0.05
KAL-R8	32	0.05	1.0	0.8	13	6	0.1	0.02	11	87	0.2	0.004	34	0.02	0.06
KAL-R9	29	0.05	0.7	0.6	19	7	0.1	0.01	7	39	0.1	0.005	35	0.01	0.25
KAL-R10	36	0.05	1.6	5.7	39	20	0.4	0.01	13	52	0.1	0.004	35	0.02	0.09
KAL-R11	32	0.05	0.7	0.7	3	20	0.1	0.01	11	51	0.1	0.003	34	0.01	0.08
KAL-R12	32	0.05	0.6	1.8	12	3	0.1	0.01	8	36	0.1	0.004	34	0.01	0.17
KAL-R13	63	0.05	2.4	0.5	31	58	0.1	0.02	34	172	0.1	0.003	34	0.01	0.06
KAL-R14	9	0.05	0.6	1.0	1	126	0.6	0.05	22	88	0.1	0.002	35	0.01	0.12
KAL-R15	12	0.05	0.5	7.1	2	82	0.3	0.02	12	33	0.1	0.002	29	0.01	0.18
KAL-R16	24	0.05	4.6	2.5	6	120	2.3	0.01	33	131	0.3	0.009	33	0.14	0.20
KAL-R17	28	0.1	4.8	71	7	242	1.8	0.01	20	140	0.2	0.008	34	0.12	0.18
KAL-R18	48	0.05	4.0	4.8	9	172	0.7	0.01	18	82	0.4	0.006	33	0.14	0.15
KAL-R19	22	0.05	3.2	1.5	5	43	0.9	0.02	10	85	0.2	0.003	34	0.09	0.11
KAL-R20	29	0.05	2.7	34	3	96	1.5	0.01	22	49	0.1	0.004	35	0.03	0.38
KAL-R21	38	0.05	0.7	2.6	19	11	0.1	0.02	12	78	0.1	0.002	35	0.01	0.34
KAL-R22	32	0.05	0.8	1.9	15	17	0.1	0.01	15	93	0.1	0.002	36	0.01	0.44
Average	44	0.23	2.7	23	39	243	1.1	0.05	46	72	0.24	0.01	34	0.07	0.18
Detection limit	0.5	0.1	0.1	0.1	1	1	0.1	0.01	1	1	0.01	0.001	0.01	0.01	
Reference materials															
STD OREAS45PA	5.1	0.9	563	19	105	1010	0.1	0.03	173	14	15	0.03	0.24	3.23	
STD DS8	27	13	112	131	323	604	5.4	0.2	281	70	2.4	0.08	0.69	0.93	

pinus halepensis (dominant species), quercus coccifera, phillyrea latifolia, genista acanthoclada, asparagus acutifolius, centaurea mixta and hymus sp. of varying age. The followed species of plants were collected and analyzed in the frame of present study: sonchus oleraceus (sample LF.EV1, LF.EV9), cichorium intybus (sample LF.EV2, LF.EV3), scolymus hispanicus (sample LF.EV4), brachypodium ramosum (sample LF.EV5, LF.EV6), erica sp. (sample LF.EV7) and sinapis arvensis (sample LF.EV8).

Soils were dried at 50°C, crumbled mechanically and then passed through a sieve with a 2 mm mesh. Samples containing large stones or clods were first sieved on a 10 mm mesh and then a 5 mm mesh. Then they were passed through a 2 mm mesh, and grains finer than 2 mm were pulverized and used for analysis. The elements Cr, Ni, Co, Mn, Cd, Cu, Zn, Pb, Fe, Mg, Zn, As, Ba, Hg, Sb, Se, Ti, Ca, P, Na, K and Al were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) after Aqua Regia Digestion, at the ACME Analytical Laboratories in Canada. The detection limit of the method was 0.1 ppm for the elements Cu, Pb, Ni, Co, Cd and Sb, 0.5 ppm for As, 1 ppm for Cr, Mn, Zn and Ba, 0.01 wt% for Fe, Ca, Mg, Al and K, 0.001 wt% for P, Ti and Na. The results of standard (STD) and black analysis (BLK) are given at the end of the Table 1.

In addition, plant samples were analyzed after cleaning and drying at 50°C. These samples were powdered in an agate mortar and analysed by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS), after Aqua Regia Digestion, at the ACME Analytical Laboratories in Canada. The detection limit of the method was 1 ppm for Mn, 0.5 for Se, 0.1 ppm for the elements Cr, Ni, Co, Zn, Cu, As, Sb and Ba, 0.01 ppm for Cu, Pb, Hg and Cd, 0.01 wt% for Ca, Al, Ti and K 0.001 wt% for P, Na, Mg and Fe. Reference material results are given at the end of the Table 2. Roots are analysed separately from the plants (Table 2). Microsoft Office XP professional was used for statistics.

Furthermore, travertine limestone samples from the Varnavas quarry and the Kalamos basin (Table 1) and Fe-Mn ore samples from the Grammatiko mine (Table 3) were dried at 50°C, pulverized and analyzed with the same method as the soil samples from the Varnavas basin. The mineralogical composition of soil and Fe-Mn ore were investigated by optical microscopy, X-ray diffraction (Siemens D5005 power diffract meter) and phase mineral analysis. XRD data were obtained using a Siemens Model 5005 X-ray diffractometer, Cu-K radiation at 40 kV, 40 nA, 0.020° step size and 1.0 sec. step time. The XRD patterns were evaluated using the EVA 2.2 program of the Siemens DIFFRAC and the D5005 software package. Polished sections prepared from soil, were examined, after carbon coating, by reflected light microscopy and scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDS) analysis. Microprobe analyses and SEM images were carried out at the University of Athens, Department of Geology and Geoenvironmemt, using a JEOL JSM 5600 scanning electron microscope, equipped with automated energy dispersive analysis system ISIS 300 OXFORD, with the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, time of measurement 50 sec and beam diameter 1-2 μm. 2 gr quantities from the soil and limestone samples were weighed and placed in porcelain crucibles in the oven at 350°C for 3 hours. The organic matter content was calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%. All weights (in duplicate) were corrected for moisture content prior to the organic matter content calculation [18, 19]. Soil pH was determined by a pH meter in a ratio of soil to de-ionized water being 1:2.5 (w/v), using a Jenway, 3040 Ion Analyser.

4. Results

4.1. Geochemistry of soil, limestone and Fe-Mn ore

The results of the soil analysis covering the Varnavas basin (Fig. 1) are presented in Table 1. The Mo, Cu, Pb, Zn, Mn, Fe, Sb, Hg contents are relatively low, whilst a significant enrichment in the metalloid As was recorded, as compared to the range of world mean values in surface soils [20]. Average values ranging from 33 to 430 ppm As, 0.3 to 2.2 ppm Mo, 14 to 39 ppm Cu, 14 to 190 ppm Pb, 39 to 270 ppm Zn, 300 to 1400 ppm Mn, 0.4 to 8 ppm Sb, 0.005 to 0.27 ppm Hg and 1.2 to 3.8 wt% Fe in the Varnavas soils are higher than in the travertine limestone in the Varnavas quarry and Kalamos basin (Table 1) and lower than in the Fe-Mn ore from Grammatiko mine (Table 3). The highest As, Zn, Hg and Mo contents were recorded in soil samples from the area of the Varnavas quarry and the highest Cu, Mn and Fe contents in the Drazaiza area (Fig. 1). The organic matter in the soil samples ranges from 0.6 to 6.7 wt% (average 2.1) and in the travertine limestone from 0.05 to 0.44 wt% (average 0.18) and pH ranges from 8.0 to 8.3 (average 8.1) (Table 1). There is a significant positive correlation between As and Cu, Zn, Sb and Fe (Table 4).

4.2. Mineralogical composition

Calcite is the most common authigenic mineral in the travertine limestone of the Varnavas quarry and the Kalamos basin, forming fine uniform micritic aggregates. Clastic dominated minerals are quartz, muscovite, clinochlore, illite (Fig. 3; Table 5). Fine-grained minerals, filling pores of the limestone, such as sulfides (pyrite, galena), sulfosalts [$Cu_4(As,Fe,Sb)_2S_5$], rutile, sphene, zircon, (Ce,La,Nd)-REE minerals and albite are common as well. Quartz, both fine-grained (Fig. 3 a, b, g) and coarse-grained (Fig. 3 h), goethite and Fe-Mn-oxides occur between calcite grains. A salient feature of the As-bearing travertine limestone at the Varnavas

Table 2. Major and trace element contents in plants from the Varnavas basin.

Sample						ppm					%	
Shoots	As	Mo	Cu	Pb	Zn	Mn	Sb	Hg	Cr	Ni	Ca	Fe
LF.EV1	1.1	1.03	16	0.9	47	84	0.05	0.016	8.4	7.1	2.39	0.13
LF.EV2	1.3	0.71	14	1.7	110	42	0.2	0.017	2.4	1.9	1.47	0.05
LF.EV3	1.5	0.72	12	1.6	99	31	0.24	0.021	1.9	1.3	2.4	0.04
LF.EV4	2.2	0.32	24	2.8	66	34	0.2	0.003	3.6	3	1.83	0.10
LF.EV5	7.7	0.8	7.7	1.5	59	120	0.4	0.005	2.8	6.8	1.9	0.06
LF.EV6	24	1.72	6.6	5.1	58	250	1	0.015	4.9	7.3	1.43	0.19
LF.EV7	28	2.12	18	7	150	270	1.3	0.03	5.4	7.3	2.13	0.25
LF.EV8	6.1	1.6	6.8	1.8	57	77	0.3	0.019	1.8	2.4	4.2	0.07
LF.EV9	7.6	3.81	8.19	0.97	27	37	0.5	0.049	1.27	2.98	2.51	0.09
Average	8.8	1.43	12.6	2.60	74.8	105	0.47	0.02	3.61	4.45	2.25	0.11
Roots												
LF.EV21	0.8	1.61	10	0.64	39	43	0.04	0.002	8.8	6.1	1.18	0.11
LF.EV22	1.4	0.83	13	2	53	23	0.11	0.002	2.7	2	0.83	0.11
LF.EV23	1.3	0.79	12	1.8	49	21	0.12	0.002	2.5	2.1	0.79	0.09
LF.EV24	1.6	0.44	71	1.7	66	35	0.16	0.0005	3	2.7	1.23	0.06
LF.EV25	70	0.93	13	14	130	200	2.83	0.0005	11	20	2.55	0.07
LF.EV26	110	1.66	110	32	160	410	4.86	0.035	20	24	4.83	0.48
LF.EV27	10	0.72	6.8	1.7	39	52	0.45	0.064	2.7	2.1	0.41	0.88
LF.EV28	8.6	1.19	8.8	1.1	40	30	0.32	0.0005	2.5	1.9	1.01	0.08
LF.EV29	6.8	4.5	6.8	0.51	23	15	0.4	0.071	1.32	2.63	1.28	0.07
Average	23.4	1.41	27.9	6.16	66.6	92	1.03	0.019	6.1	7.1	1.56	0.22
Detection limit	0.1	0.01	0.01	0.01	0.1	1	0.02	0.015	0.1	0.1	0.01	0.25
Reference materials												
STD V14	11.6	0.07	4.65	1.02	14.2	2153	0.07	0.051	1.1	1.4	0.62	0.02
STD V16	1.6	1.65	6.53	2.94	37.4	757	0.08	0.038	378.9	8.3	0.3	0.46

Table 3. Major and trace element contents in the Fe-Mn ore from the Grammatiko mine.

Sample				ppm					%
	As	Mo	Cu	Pb	Zn	Mn	Sb	Hg	Fe
G.ER.109	920	20	1600	2900	3300	>10000	1300	6.2	26.0
G.ER.101	58	0.7	1.2	21	154	>10000	15	0.06	40.0
G.ER.108	1600	14	>10000	7200	900	1700	400	20	5.3
Average	860	12	3870	3370	1450	7230	570	8.8	23.8
Detection limit	0.5	0.1	0.1	0.1	1	1	0.1	0.01	0.01
Reference materials									
STD DS8	26	13.44	110	123	312	615	4.8	0.192	2.46
STD OREAS45CA	3.8	1	494	20	60	943	0.13	0.03	15.69

basin is the occurrence of fossilized micro organisms, resembling foraminifera, commonly as fragments (Fig. 3 e, f), having the composition of hydrous Fe-Mn-oxides (Table 5). Arsenic and magnesium in calcite were not detected, using EDS (lower than detection limits).The most abundant minerals in the Fe-Mn ore from the Grammatiko mine are hematite, goethite, pyrolusite and veins of calcite cross-cutting the ore. Hematite contains traces of As, Zn and Ba (Fig. 4; Table 6). The pyrolusite appears with a leafy structure (Fig. 4). Iron-Mn oxides and hydroxides with a varying Fe/Mn ratio form flakes, tiny spheroid aggregates, micronodules or concretions. The arsenic content in hydrous Fe-oxides is higher, compared to the Mn-oxides, which are commonly As-free (Table 6).

4.3. Trace element contents in plants

Plants from the Varnavas quarry showed higher As and heavy metal contents (Mo, Mn, Fe, Cu, Zn, Hg, Pb, Sb) than those outside the quarry area (Ntrazaiza, Pourithi)

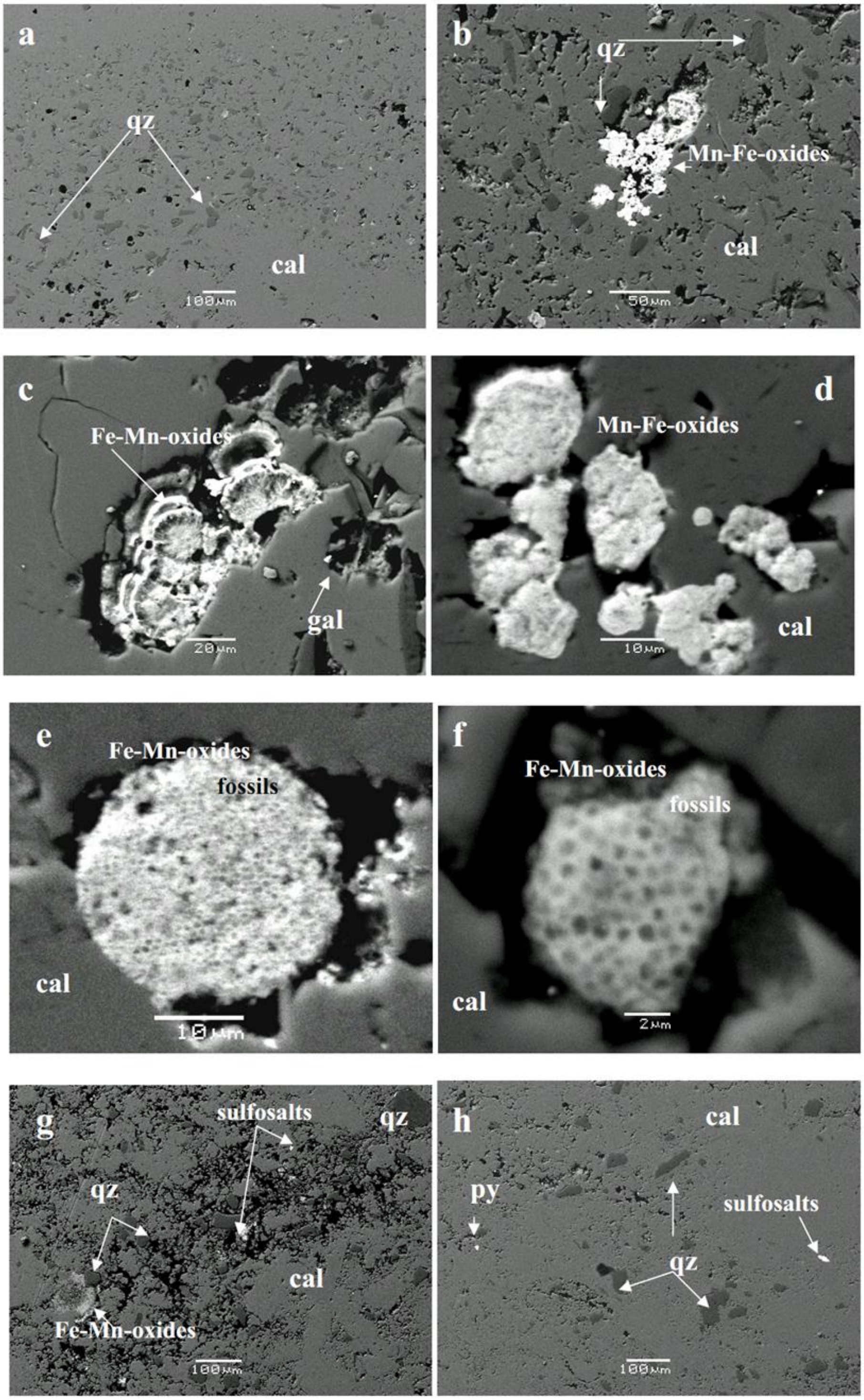


Figure 3. Selected backscattered images from the Varnavas travertine limestone quarry showing calcite (cal) forming fine uniform micritic aggregates. Quartz occurs as fine-and coarse-grained (Figure 3 a, b, g, h) between calcite grains. Mn-Fe-oxides, and Fe-Mn-oxides (Figure 3 b-h) and fossilized microorganisms, having the composition of hydrous Fe-Mn-oxides (Figure 3 e, f). fine-grained sulphides [galena (gal) and pyrite (py)] and sulfosalts [$Cu_4(As,Fe,Sb)_2S_5$]. The chemical composition of minerals is given (Table 5).

Table 4. Correlation matrix of selected major and trace elements in soils from the Varnavas basin (Tab. 1).

	As	Mo	Cu	Pb	Zn	Mn	Sb	Hg	Ba	Sr	Fe	P	Ca	Al
As	1.00													
Mo	0.74	1.00												
Cu	0.19	0.22	1.00											
Pb	0.44	-0.15	-0.20	1.00										
Zn	0.66	0.08	0.05	0.87	1.00									
Mn	0.53	0.39	0.82	0.08	0.39	1.00								
Sb	0.87	0.51	-0.12	0.71	0.71	0.22	1.00							
Hg	0.80	0.42	-0.11	0.62	0.79	0.25	0.74	1.00						
Ba	0.41	-0.10	0.16	0.83	0.70	0.33	0.63	0.43	1.00					
Sr	-0.59	-0.42	-0.47	-0.46	-0.44	-0.62	-0.60	-0.31	-0.70	1.00				
Fe	0.52	0.52	0.92	-0.04	0.24	0.88	0.22	0.16	0.25	-0.67	1.00			
P	-0.34	-0.25	0.73	-0.28	-0.28	0.36	-0.44	-0.51	0.06	-0.17	0.45	1.00		
Ca	-0.14	-0.10	-0.68	-0.08	-0.02	-0.59	-0.14	0.20	-0.52	0.78	-0.67	-0.62	1.00	
Al	-0.26	-0.16	0.80	-0.15	-0.15	0.49	-0.36	-0.45	0.21	-0.41	0.62	0.78	-0.74	1.00

(Fig. 5). Elevated Mo, As, Mn, Sb and As contents were recorded in plants from the quarry (Table 7 & Table 8). The degree of accumulation in Mn, Cu, Zn, Pb and Sb is medium and low in As and Fe [21]. More specifically, average values of shoots ranged from 1.1 to 28 ppm As, 0.3 to 2.1 ppm Mo, 6.6 to 24 ppm Cu, 1.5 to 11 ppm Pb, 47 to 150 ppm Zn, 34 to 266 ppm Mn, 0.08 to 1.3 ppm Sb, 0.003 to 0.3 ppm Hg and 0.05 to 0.25 wt% Fe in the Varnavas basin. Average values of roots ranged from 0.8 to 114 ppm As, 0.44 to 1.7 ppm Mo, 6.75 to 105 ppm Cu, 0.64 to 32 ppm Pb, 39 to 157 ppm Zn, 23 to 411 ppm Mn, 0.04 to 4.9 ppm Sb, 0.5 to 64 ppb Hg and 0.06 to 0.88 wt% Fe. Although the translocation factor (the percentage of the metals translocated from roots to shoots) is relatively low, ranging from 0.11% to 2.8% (average 0.33%), the accumulation factor for As, Cr, Ni, Mn, Fe, Sb, Zn, Cu and Hg in plants [(% metals in plants×100)/metal in soil] exhibits a wide range from relatively low (5.2–9.0% for As, Fe, Cr, Ni and Pb), much higher (56 - 67% for Cu and Zn) and exceptionally high (160% for Mo). (Table 7). Also, a significant correlation between the translocation factors of Fe and As (Fig. 5 b) is remarkable.

5. Discussion

The investigation of the As, Mo, Cu, Pb, Zn, Mn, Fe, Sb and Hg level at the travertine limestone of the Varnavas quarry and the associated soils revealed the presence of elevated As contents in the travertine limestone, up to 210 ppm while As in the associated soils increases (up to 430 ppm) by a factor of approximately 2 (Table 1), falling in the field of highly polluted soils [6, 7].

Calcite is the most common authigenic mineral in lakes, dominated by inorganic precipitation, whilst marine calcite is predominantly biogenic [22]. Arsenic in nature is commonly found as arsenite, [As(III)] at moderately and strongly reduced conditions and arsenate, [As(V)] in the aerobic environment [23]. Thus, the speciation of arsenic could be used to determine the dominant redox and pH conditions, driving the cation exchange reactions and dissolution of carbonates and silicates [4, 24]. However, more recent studies do not support this, as the redox kinetics are slow and the redox potential tends to be controlled by other major elements [25, 26]. Experimental data indicated that arsenate ions show great affinity for calcite surface sites at pH 8.3 and that uptake rate decreases, in time, with saturation of sites at higher As(V) concentrations in solution [27]. A diversity of surface site preferences among tetrahedral oxyanions suggests that factors other than size and charge are responsible for site-specific interactions at the calcite surface. The lack of any correlation between As and Ca, the positive As-Fe correlation ($r = 0.7$) and the relatively high As content in Fe-Mn oxides at the Varnavas and Kalamos travertine limestones (Table 4 & Table 5; Fig. 5) may suggest that arsenic is mostly hosted in hydrous Fe-Mn-oxides, whilst in calcite it is lower than detection limit (EDS method).

5.1. Source for As and heavy metals at the Varnavas limestone quarry and soils

The Varnavas travertine limestone basin, composed of lacustrine and fluvial sediments, is characterized by a significant enrichment in the metalloid As in soil samples ranging from 33 to 430 ppm (Table 1). The majority of the As values exceeds the maximum permitted limits of 55 ppm in soils and also exceeds common As contents in sedimentary rocks [6, 7, 28]. The terrestrial weathering processes of the Grammatiko deposit and related rocks

Table 5. Representative microprobe analyses of Mn-Fe-oxides and arsenides from the travertine limestone of the Varnavas and Kalamos basins.

	Varnavas basin														
wt%	Hydrous Mn-Fe-oxides							Hydrous Fe-Mn- oxides							
SiO_2	1.1	1.2	0.9	6.3	1.3	0.6	1.2	2.4	3.7	2.2	2.8	6.4	1.5	3.2	4
Al_2O_3	17.1	15.5	10.65	6.6	4.4	n.d.	3.4	4.9	5.2	4.8	4.7	6	3.1	3	4.2
As_2O_3	1.3	1.7	1.27	1.7	1.5	n.d.	1.4	2.3	2.6	2.7	3.4	1.4	1.3	n.d	n.d
Fe_2O_3	6	5.8	7.6	9.1	4	2.8	1.2	65.9	52.6	54.3	60.8	7.5	2.8	8	8.9
TiO_2	n.d.	0.4	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	6.1	0.4	n.d.	0.7	n.d	0.6	n.d
CaO	2.5	2.7	5.4	3.9	3.3	2.1	3.4	2.1	2.1	4.9	3.6	4.8	3.6	5.7	6.5
MnO	41.9	44.1	40.76	41.7	54.6	56.5	55.1	n.d.	0.4	0.5	n.d.	39.4	53.6	44.1	40.2
NiO	2.3	2.1	1.3	0.6	1.1	n.d.	1.1	n.d.	n.d.	n.d.	n.d.	n.d	n.d	n.d	n.d
ZnO	2.5	2.1	1.3	0.6	1.4	n.d.	0.8	n.d.	n.d.	n.d.	n.d.	n.d	1	0.8	1.3
BaO	1.8	2.2	3.43	4.9	6.1	12.6	5.8	n.d.	n.d.	n.d.	n.d.	7.6	8.8	5.8	4.9
PbO	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	8.2	7.7
Total	76.3	77.8	73.11	75.4	77.7	74.6	73.4	77.6	72.7	69.8	75.3	74.1	75.7	79.4	77.7
Cont.	Kalamos basins														
wt%	Hydrous Mn-Fe-oxides			Hydrous Fe-Mn- oxides											
SiO_2	1.6	0.8	1.1	2.0	3.8	3.1	3.4	3.8	4.6	2.8	4.6				
Al_2O_2	2.9	1.3	2.2	n.d.	n.d.	n.d.	n.d.	6.0	4.2	5.8	4.2				
As_2O_3	n.d	n.d	n.d	0.9	n.d	0.8	n.d	1.5	1.3	2.0	1.3				
Fe_2O_3	16.1	7.6	10.1	33.4	62.6	54.1	79.4	44.8	68.1	56.3	68.1				
Cu_2O	n.d	n.d	n.d	n.d	n.d	1.5	n.d	n.d	n.d	n.d	n.d				
TiO_2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.7	0.7	0.7				
SO_4	0.8	n.d	n.d	1.6	0.7	1.8	0.5	0.5	0.5	1.0	0.5				
CaO	7.1	12.7	5.1	22.4	10.8	14.7	2.2	16.1	4.0	8.7	3				
MnO	31.8	37.1	43.6	n.d	0.3	2.8	n.d	1.7	n.d	n.d	n.d				
NiO	0.4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d				
BaO	6.1	6.0	10.1	n.d	n.d	0.5	n.d	n.d	n.d	n.d	n.d				
Total	66.8	65.5	72.2	60.3	78.2	79.3	85.5	74.4	83.4	77.3	82.4				
	Sulfosalts -Varnavas basin														
Cont.	1	2	3	4	5										
Fe	6.8	2.6	2.6	2.7	5.5										
Cu	44.1	41.2	43.5	43.8	39.4										
Sb	n.d.	n.d.	n.d.	n.d.	16.8										
Zn	n.d.	n.d.	n.d.	n.d.	2.5										
Mn	0.6	4.1	4.2	4.2	n.d.										
As	20.8	22.6	21.3	21.5	8.7										
S	27.9	28.9	27.6	27.9	25.8										
Total	100.2	99.4	99.2	100.1	98.7										

Table 6. Representative microprobe analyses of Mn-Fe-oxides from the ore of Grammatiko mine.

	G.ER.101			G.ER.108			G.ER.109			G. SK.5		G. SK.4	
wt%	goeth	hem	hem	hem	hem	pyr	pyr	hem	hem	goeth	goeth	goeth	goeth
Al_2O_3	0.4	n.d.	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.5	0.4	0.3	0.5
SiO_2	2	1.6	1.9	3.4	3.2	n.d	0.4	1.6	1.5	2.5	1.8	1.5	1.5
CaO	0.6	0.7	0.6	1.1	1	0.7	0.9	0.7	0.6	1.9	1.6	0.9	0.9
Fe_2O_3	75.2	90.2	89.7	89.9	93.7	n.d	1.3	75.5	79.2	75.5	77.5	76.2	73.2
MnO	1.3	3.5	3.3	1.3	n.d	81.7	69.8	16.7	14.2	2.2	1.5	4.7	5.2
As_2O_3	2	1.5	1.3	n.d	n.d	n.d	n.d	n.d	n.d	0.8	1.1	1.1	0.9
ZnO	6.3	n.d	1.7	n.d	n.d	n.d	2.9	1.2	n.d	n.d	0.6	n.d	n.d
K_2O	n.d	n.d	n.d	n.d	n.d	n.d	3.9	0.3	n.d	n.d	n.d	n.d	n.d
TiO_2	n.d	n.d	n.d	n.d	n.d	n.d	0.5	n.d	n.d	n.d	n.d	n.d	n.d
MgO	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.7	0.6	n.d	0.7
Total	87.8	97.5	98.5	95.7	97.9	82.4	79.7	96	95.5	84.1	85.1	83.7	82.9

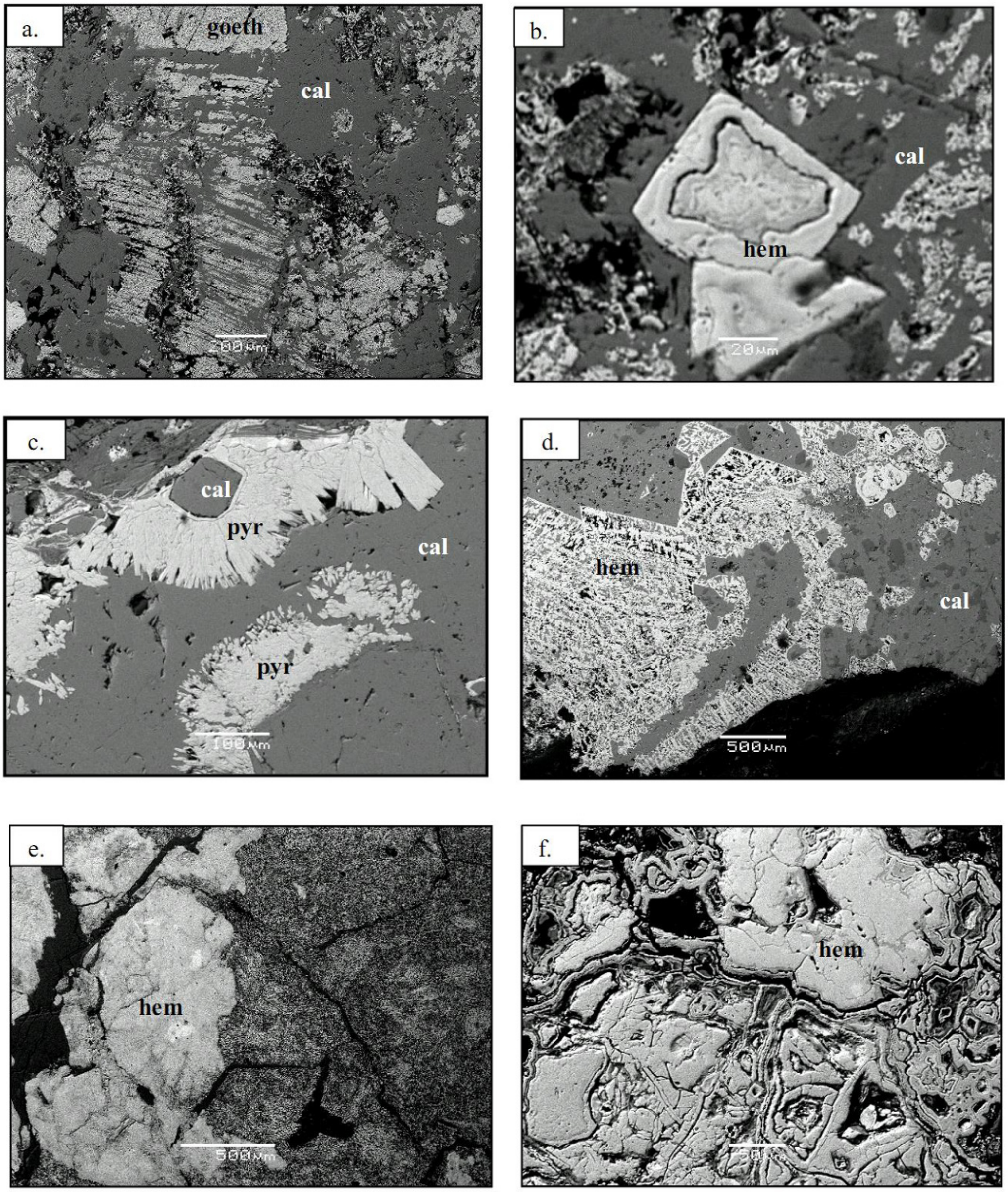
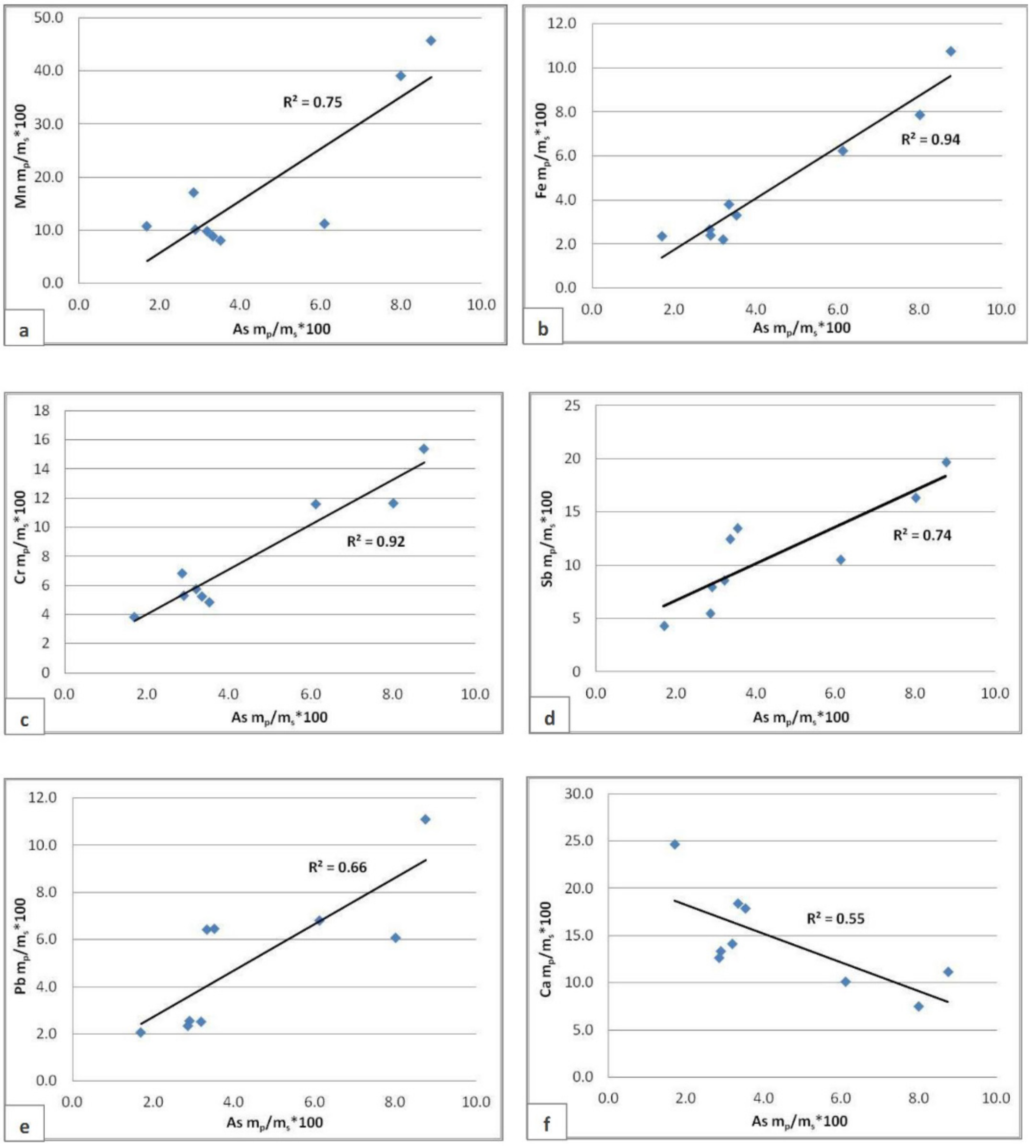


Figure 4. Selected backscattered images from the Grammatiko mine showing goethite (goeth) (4a), hematite (hem) (4b, e, f), and pyrolusite (pyr) (4c) and calcite (cal). The chemical composition of minerals is given (Table 6).

may be a source for manganese and arsenic into the lakes and depositional basins of Attica. Manganese is probably transported in river water as colloids and as a soluble form of the Mn (II) species [29]. A salient feature of the As-bearing travertine limestone in the Varnavas basin is the occurrence of fossilized microorganisms, resembling foraminifera (Fig. 3 e, f), which have a composition of hydrous Fe-Mn-oxides. Lakes do not commonly contain forams, although some species may survive if introduced into coastal lakes or basins with near sea water salinities. Marine transgressions over the barrier, or subsurface seepage of seawater through the barrier have been proposed as the origin for saline conditions in these basins, and therefore a significant source of water, influencing both water level and water composition [30]. In addition to the river discharge a contribution of seawater at a coastal zone may lead to deposition of dissolved manganese and iron carried



Symbols: m_p= metal content in plant; m_s = metal content in soil

Figure 5. Variation of the accumulation factor [(metals in plants x 100)/metal in soil] for Mn, Fe, Cr, Sb, Pb and Ca versus that for arsenic in the Varnavas quarry. Data from Table 7; where symbol m_p is the metal content in plant and m_s is the metal content in soil.

by water, as it is exemplified by the presence, mostly as fragments, of fossilized microorganisms in travertine limestone (Fig. 3), [31]. The deposition of hydrous Mn-Fe oxides (Fig. 3; Table 5) seems to play an important role in controlling the As contents in travertine limestone. Also, it has been suggested that the ocean is an important natural sink of As with median concentrations in oceanic sediments about an order of magnitude higher than those observed on land [6, 32].

5.2. Bio-accumulation of As and heavy metals

Arsenic contents in plants grown on soils with the elevated As content of the Varnavas quarry are higher compared to those from the Drazaiza area, outside the quarry (Table 1, Table 2 and Table 7), and fall within the range (5-20 ppm) of the phytotoxicity [20]. Also, the increasing trend of the As content in plants with the As level in corresponding soils, and the relatively low translocation factor (the

Table 7. Major and trace elements in soils and corresponding plants from the Varnavas basin, Attica, and the percentage of soil metals in plants. Data from Table 1 and Table 2.

		ppm										%wt	
Location	Description	As	Mo	Cu	Pb	Zn	Mn	Sb	Hg	Cr	Ni	Ca	Fe
Drazaiza	LF.EV1	1.1	1.03	16	0.9	47	84	0.05	0.016	8.4	7.1	2.39	0.13
	LF.ES1	33	0.6	39	14	64	940	0.4	0.01	160	81	13	3.4
	m_p/m_s*100	3.3	171.7	41.0	6.4	73.4	8.9	12.5	160	5.3	8.8	18.4	3.8
Pourithi	LF.EV2	1.3	0.71	14	1.7	110	42	0.2	0.017	2.4	1.9	1.47	0.05
	LF.ES2	45	0.5	20	66	120	410	2.5	0.03	45	55	11	2.1
	m_p/m_s*100	2.9	142	70	2.6	91.7	10.2	8	56.7	5.3	3.5	13.4	2.4
	LF.EV3	1.5	0.72	12	1.6	99	31	0.24	0.021	1.9	1.3	2.4	0.04
	LF.ES3	47	0.5	16	63	109	314	2.8	0.04	33	44	17	1.8
	m_p/m_s*100	3.2	144	75	2.5	90.8	9.9	8.6	53	5.8	3.0	14.1	2.2
	LF.EV4	2.2	0.32	24	2.8	66	34	0.2	0.003	3.6	3	1.83	0.1
	LF.ES4	36	0.3	15	41	80	300	1.9	0.01	31	48	18	1.6
	m_p/m_s*100	6.1	106.7	160	6.8	82.5	11.3	10.5	30	11.6	6.3	10.2	6.3
Varnavas quarry	LF.EV5	7.7	0.8	7.7	1.5	59	120	0.4	0.005	2.8	6.8	1.9	0.06
	LF.ES5	270	1	19	64	180	700	7.3	0.13	41	54	15	2.4
	m_p/m_s*100	2.9	80	40.5	2.3	32.8	17.1	5.5	3.8	6.8	12.6	12.7	2.7
	LF.EV6	24	1.72	6.6	5.1	58	250	1	0.015	4.9	7.3	1.43	0.19
	LF.ES6	300	0.9	18	84	240	640	6.1	0.19	42	53	19	2.4
	m_p/m_s*100	8	191.1	36.7	6.1	24.2	39.1	16.4	7.9	11.7	13.8	7.5	7.9
	LF.EV7	28	2.12	18	7	150	270	1.3	0.03	5.4	7.3	2.13	0.25
	LF.ES7	320	1	19	63	240	590	6.6	0.18	35	52	19	2.3
	m_p/m_s*100	8.8	212	94.7	11.1	62.5	45.8	19.7	16.7	15.4	14.0	11.2	10.8
	LF.EV8	6.1	1.6	6.8	1.8	57	77	0.3	0.019	1.8	2.4	4.2	0.07
	LF.ES8	360	0.9	23	86	260	710	7	0.21	47	64	17	2.9
	m_p/m_s*100	1.7	177.8	29.6	2.1	21.9	10.8	4.3	9.0	3.8	3.8	24.7	2.4
	LF.EV9	7.6	3.81	8.19	0.97	27	37	0.5	0.049	1.27	2.98	2.51	0.09
	LF.ES12	216	2.2	21	15	39	451	3.7	0.03	26	36	14	2.72
	m_p/m_s*100	3.5	173.2	39.0	6.5	69.2	8.2	13.5	163.3	4.9	8.3	17.9	3.3

Symbols: m_p= metal content in plant; m_s = metal content in soil

percentage of the metals translocation from roots to shoots ranging from 0.11% to 2.8% in the Varnavas basin are comparable to those reported elsewhere [33, 34]. Although the accumulation factor [(% metals in plants × 100)/metal in soil] for As, Fe, Cr and Ni, ranging from 4.8% to 9% is lower than that for Cu, Zn and Hg, ranging from 41% to 67%, and the exceptionally high, average 160% for Mo (Table 7) the accumulation of arsenic mostly in shoots of plants, coupled with published data elsewhere may suggest that certain plants are potentially useful in phytoremediation [6, 33]. Moreover, the significant correlation between the translocation factors for Fe and As (Fig. 5 c), coupled with the association of As with Fe oxides/hydroxides (Table 5) confirms that the latter represent the major sorbing agents for As in soils and that increased As solubility under reduced conditions is associated with dissolution of Fe and Mn oxides/hydroxides [5]. Therefore, the presented geochemical data on soil, corresponding plants and travertine limestone itself point to a potential environmental risk and health effects.

6. Conclusions

The presented geochemical data on soils, corresponding plants and travertine limestone itself, coupled with geological and phase mineral data from the Varnavas and Kalamos basins and literature data, lead to the

Table 8. Correlation matrix of selected major and trace elements in the percentage of bioaccumulation from the Varnavas basin (Table 7).

		As	Mo	Cu	Pb	Zn	Mn	Sb	Hg	Cr	Ni	Ca	Fe
		m_p/m_s*100											
As	m_p/m_s*100	1											
Mo		0.26	1										
Cu		0.50	-0.22	1									
Pb		0.82	0.45	0.35	1								
Zn		0.12	-0.07	0.67	0.25	1							
Mn		0.73	0.29	0.08	0.44	-0.42	1						
Sb		0.86	0.54	0.30	0.91	0.32	0.49	1					
Hg		-0.09	0.30	0.15	0.28	0.77	-0.62	0.35	1				
Cr		0.94	0.06	0.58	0.68	0.02	0.80	0.66	-0.34	1			
Ni		0.63	0.06	-0.14	0.64	-0.33	0.68	0.56	-0.31	0.61	1		
Ca		-0.83	0.13	-0.45	-0.40	0.00	-0.68	-0.53	0.35	-0.85	-0.47	1	
Fe		0.93	0.38	0.38	0.87	-0.06	0.77	0.79	-0.18	0.90	0.70	-0.66	1

Symbols: m_p = metal content in plant; m_s = metal content in soil

following conclusions:

1. Elevated As contents in the travertine limestone, ranging from 61 to 210 ppm and the associated soils, ranging from 33 to 430 ppm, fall in the field of highly polluted soils.

2. Arsenic content in soil is increased compared to that in rocks.

3. Plants are usually well protected against As uptake.

4. The soil contamination at the Varnavas quarry by As and to a lesser extent by Mn, is attributed to natural processes.

5. The Varnavas travertine limestone and soil As contamination is mostly related to the transportation and deposition of the weathered material from the neighboring Grammatiko Fe-Mn mineralization, and to a lesser extent to the marine transgressions during the evolution of the basin.

6. The connection of the quarry contamination with the mineralization of the Lavrio type is consistent with the very good positive correlations ($r = 0.7 - 0.9$) between As and Mo, Zn, Sb and Hg, and a good ($r = 0.55$) correlation between As and Mn-Fe.

7. The translocation factor is relatively low (average 0.33%), although As contents in shoots of plants ranges from 1.1 to 28 ppm As, and in roots it ranges from 0.8 to 110 ppm As.

8. The accumulation factor for As, Cr, Ni, Mn, Fe, Sb, Zn, Cu and Hg in plants exhibit a wide range from relatively low (5.2–9.0% for As, Fe, Cr, Ni and Pb), much higher (56–67% for Cu and Zn) and exceptionally high (160% for Mo).

9. A significant positive correlation between the translocation factors for Fe and As ($r = 0.7$) confirms the association of As with Fe-Mn oxides/hydroxides.

10. The presented data for the soils suggest a potential environmental risk, due to As contamination in soil and plants, for fluvial or marine depositional environments and/or those located in the vicinity of mining areas.

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